Supplementary Materials

Photovoltaic arrays as highly efficient system for biomedical and electrochemical surface-enhanced Raman Spectroscopy analysis

K. Niciński[a],, E. Witkowska[a], D. Korsak, K. Noworyta, J. Trzcinska-Danielewicz[b],

A. Girstun[b] and A. Kamińska[a]*

[a]Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52,

01-224 Warsaw, Poland

[b]Department of Molecular Biology, Institute of Biochemistry, Faculty of Biology,

University of Warsaw, 02-096 Warsaw, Poland

1 Characterization PV surfaces

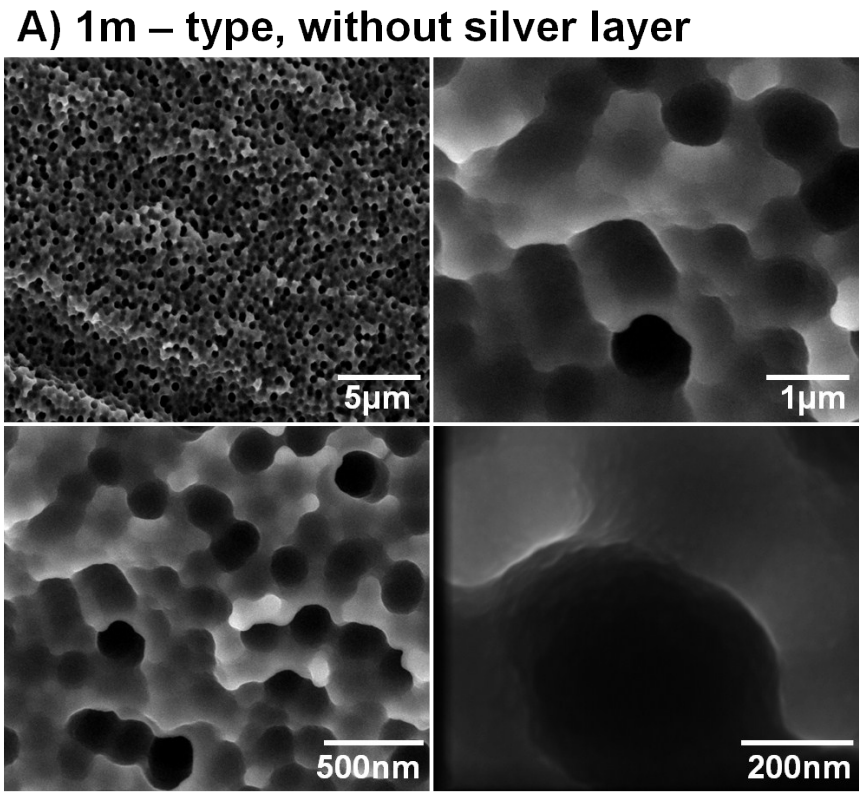
1.1. Method of PV production.

They are produced by a screen-printing process. It is similar to that used to produce the heating strips on rear and front car windscreens. In the process silver paste is squeezed through a mesh onto the cell surface. In the end it is dried and then fired at a higher temperature to drive off the organic binder in the paste and to allow the silver particles to coalesce. The middle layer p-n junction consists of either mono (hexagonal) or polycrystalline (square) silicon wafer. More than a half of module production is now based on the use of multicrystalline silicon wafers rather than those produced using the Czochralski method. This technique is basing on molten silicon being poured into a container and then allowed to cool. This are doped p-type using boron. In the next step wafers are mechanically and chemically polished to remove any damage from previous wafers creating processes. The surface is then anisotropically etched to texture the surface of the silicon. The main reason to do so is to minimise possible reflection losses and to increase the range of angles at which light rays are refracted into the silicon, what causes enhancement in the optical path length. A p-n junction are produced in the wafers in the process of diffusing phosphorus into the surface of the wafer to convert the surface to a n-type region.

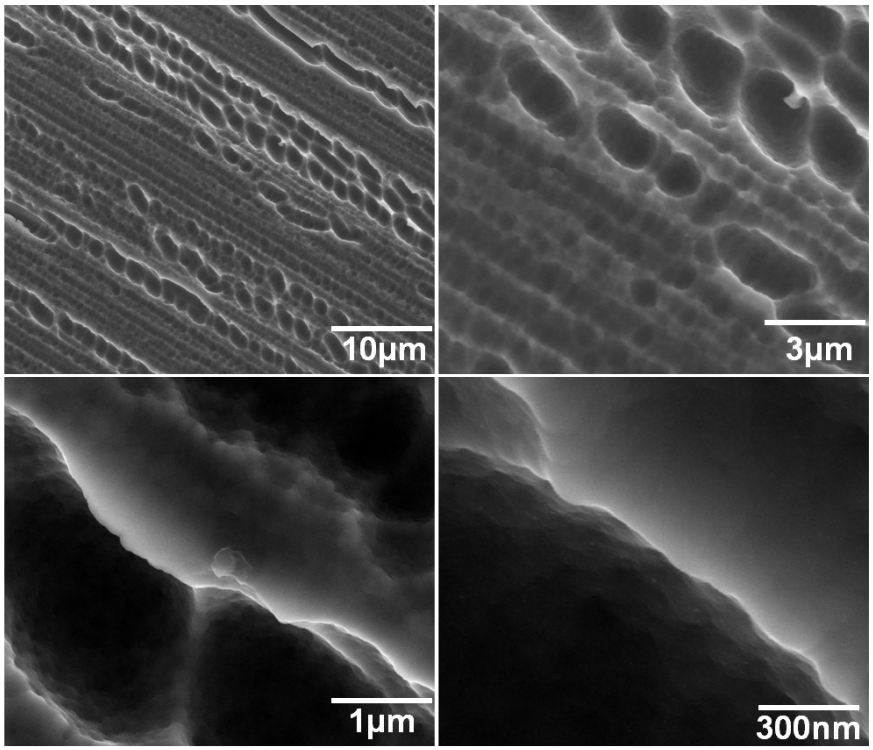
The back plate which is an electrical contact to the rear of the p-type region. It is attached by annealing an aluminium layer deposited over the back of the device. The p+ layer not only minimises the back contact resistance but introduces a ‘‘back surface field’’ to reflect minority carriers back toward the depletion region. This effect is even more enhanced by the *Passivated Emitter and Rear Cell* (PERC) technology. In the PERC technology, the back of the silicon wafer is first covered with a special layer of dielectric (insulator), which is covered with holes cut out by a laser. The metallization layer in the form of aluminum is then applied to the dielectric, so that the silicon wafer contacts the metal only through microscopic holes.

The main task of PERC technology is to increase the efficiency of the cell thanks to the dielectric layer, which reflects every light reaching the bottom layer of the plate without generating the electron back into the cell. Through this reflection, photons basically have a second chance to generate electricity.

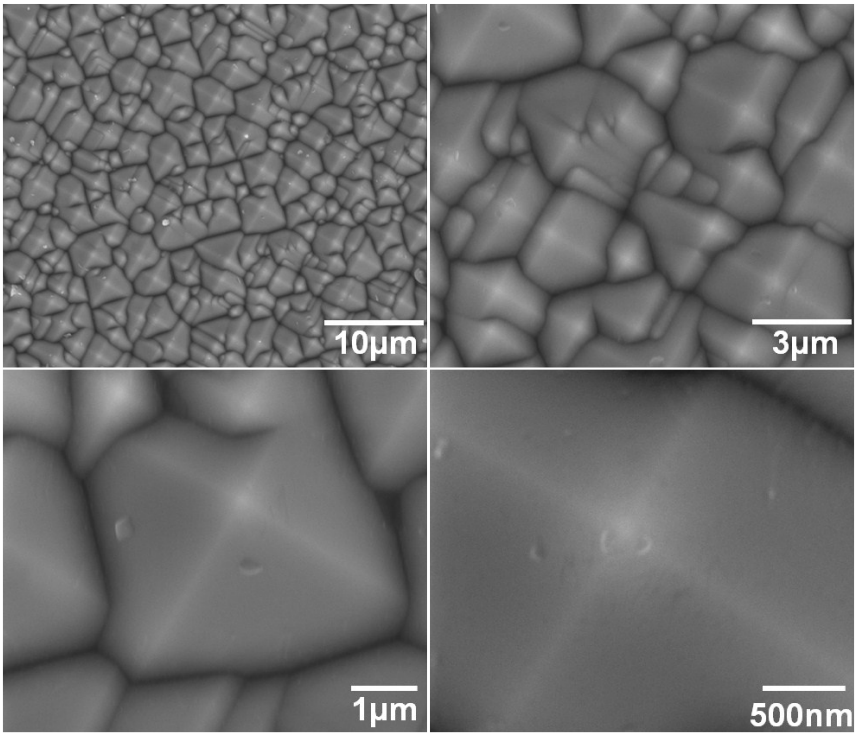
1.2. SEM and AFM measurements



B) 1 – type, without silver layer



C) 2 – type, without silver layer



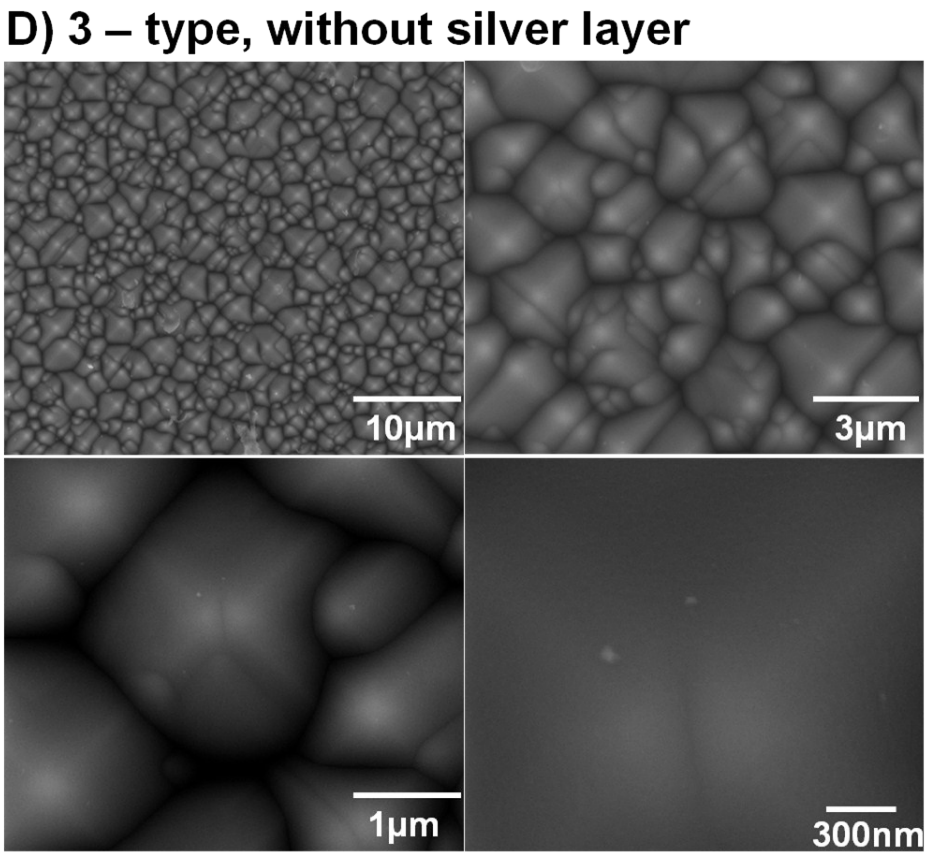
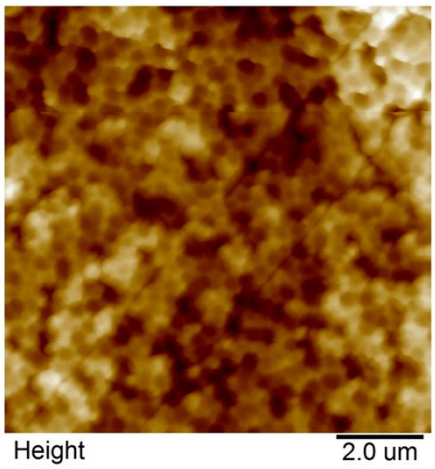
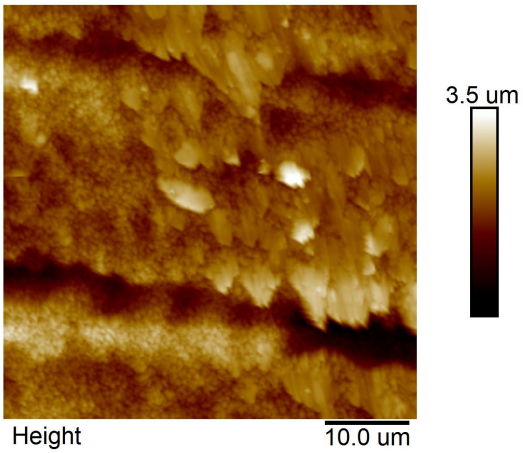


Fig. S1. SEM images at four magnifications of four testes PV samples named 1m, 1, 2, and 3.

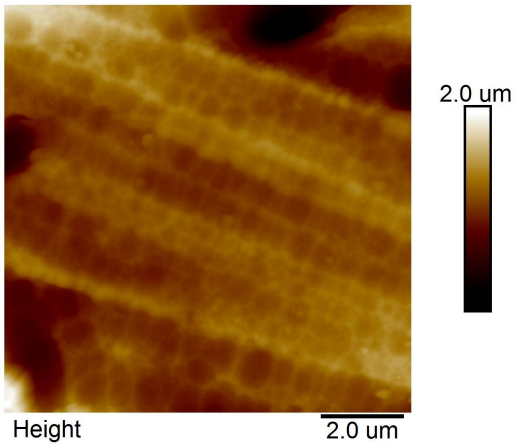
A) Type - 1m

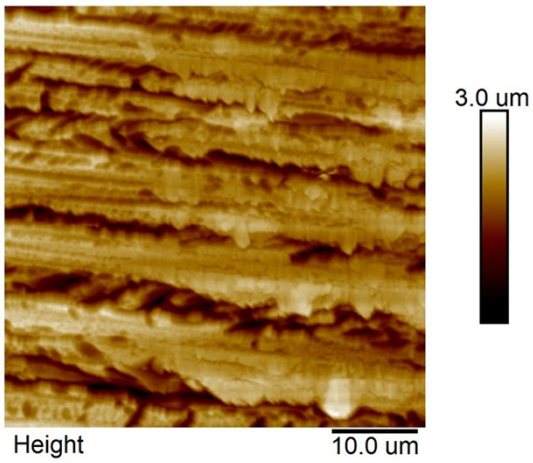




Roughness (R_a):120 ± 6 nm

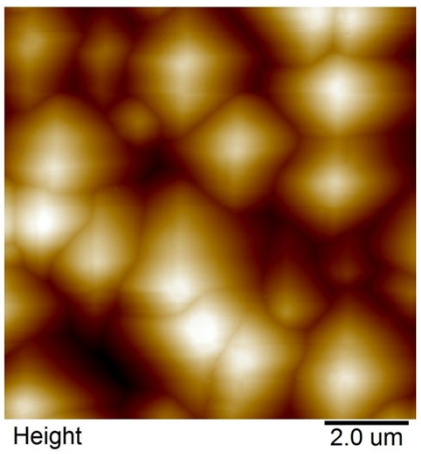
B) Type - 1

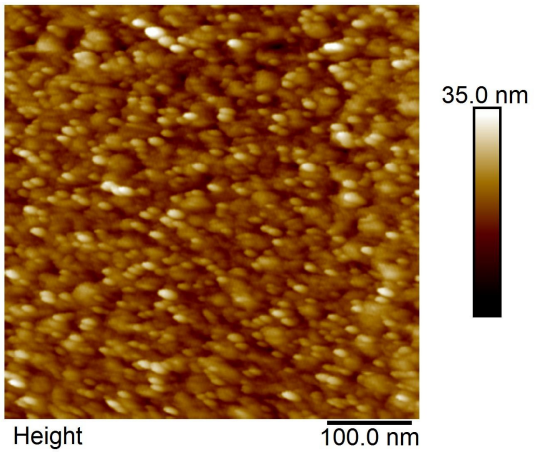




Roughness (R_a): 239 ± 21 nm

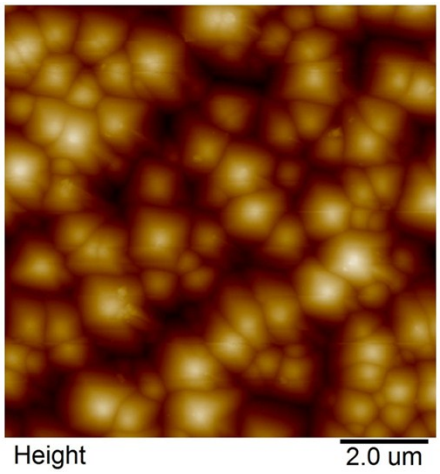
C) Type - 2

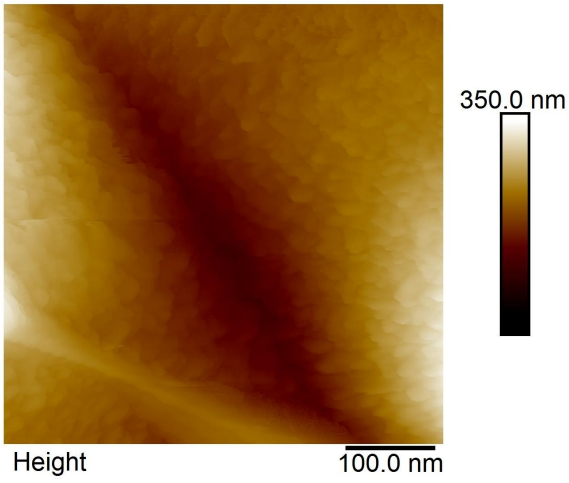




Roughness (R_a): **364 ± 58 nm**

D) Type - 3



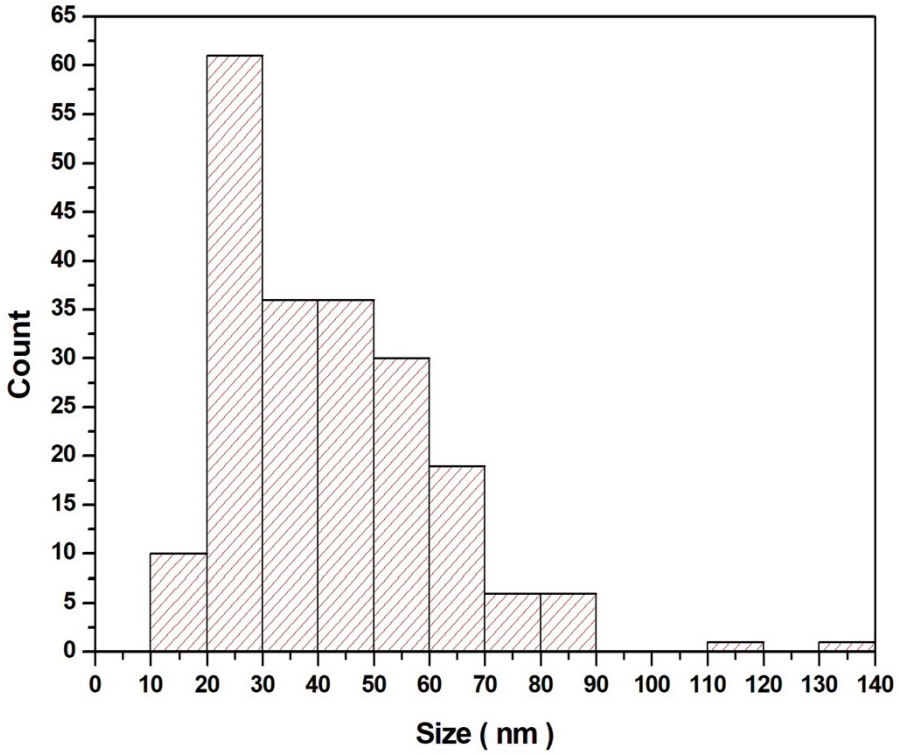


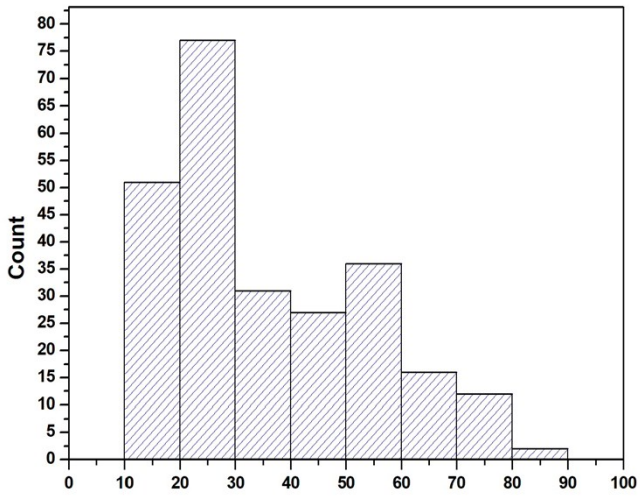
Roughness (R_a): **213 ± 5 nm**

Fig. S2. AFM images at different magnifications of Ag/PV SERS-active platforms sputtered with 8 nm layer of silver via PVD technique.

A) Sample 1-type

Count: 206
Median: 41.85
StdDev:18.9





C) Sample 3-type

Count: 288
Median: 34.58
StdDev: 17.9

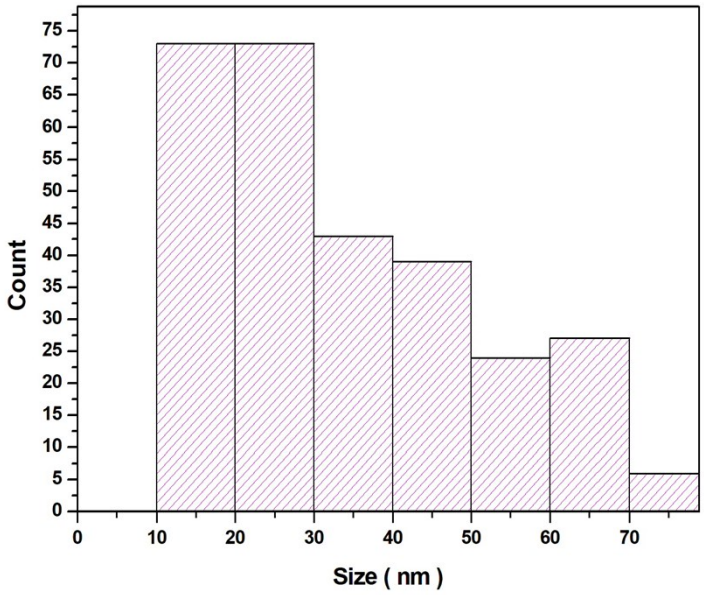


Fig. S3. Histograms of the size of the silver objects on the surface of the PV based substrates.

Ion etched Si

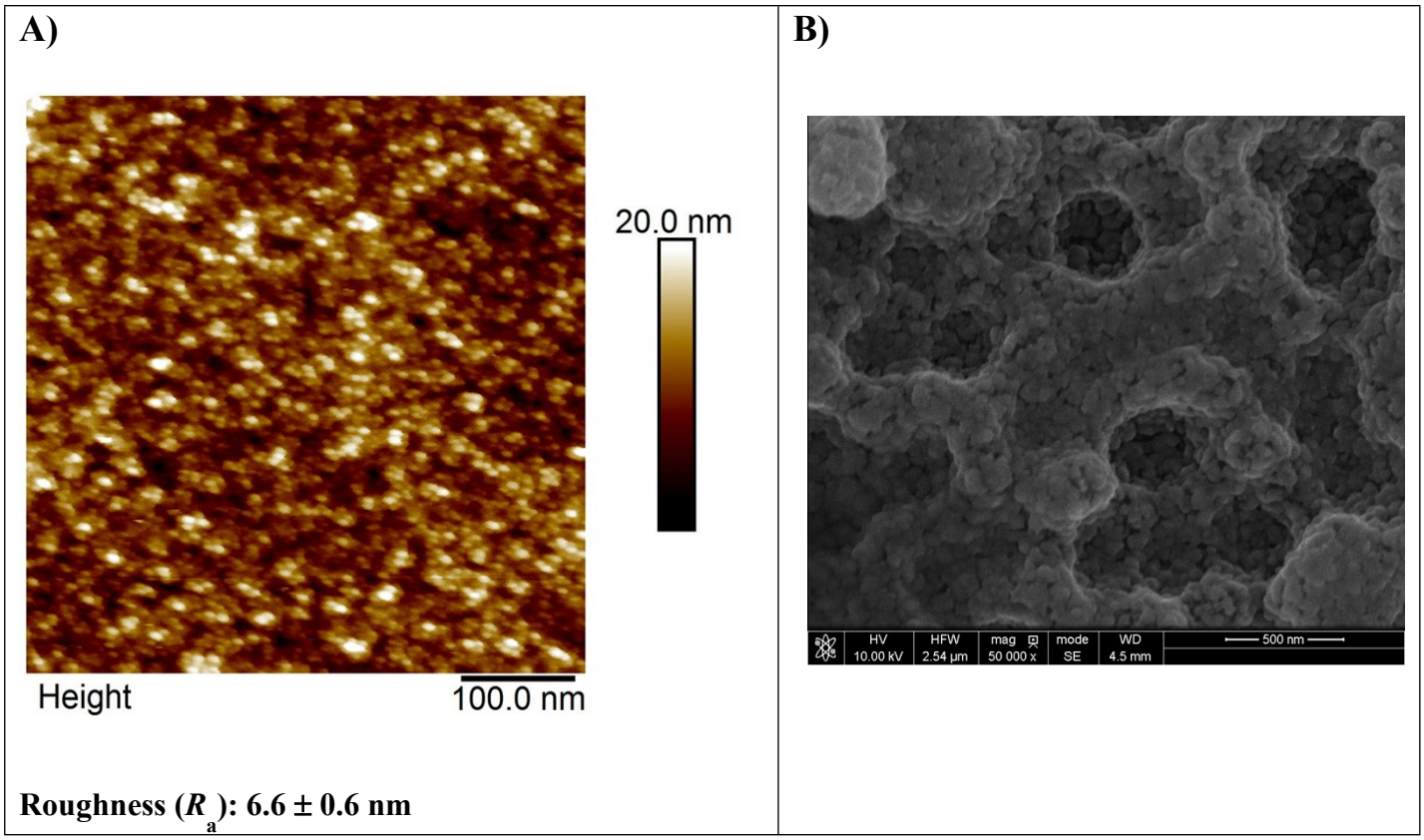
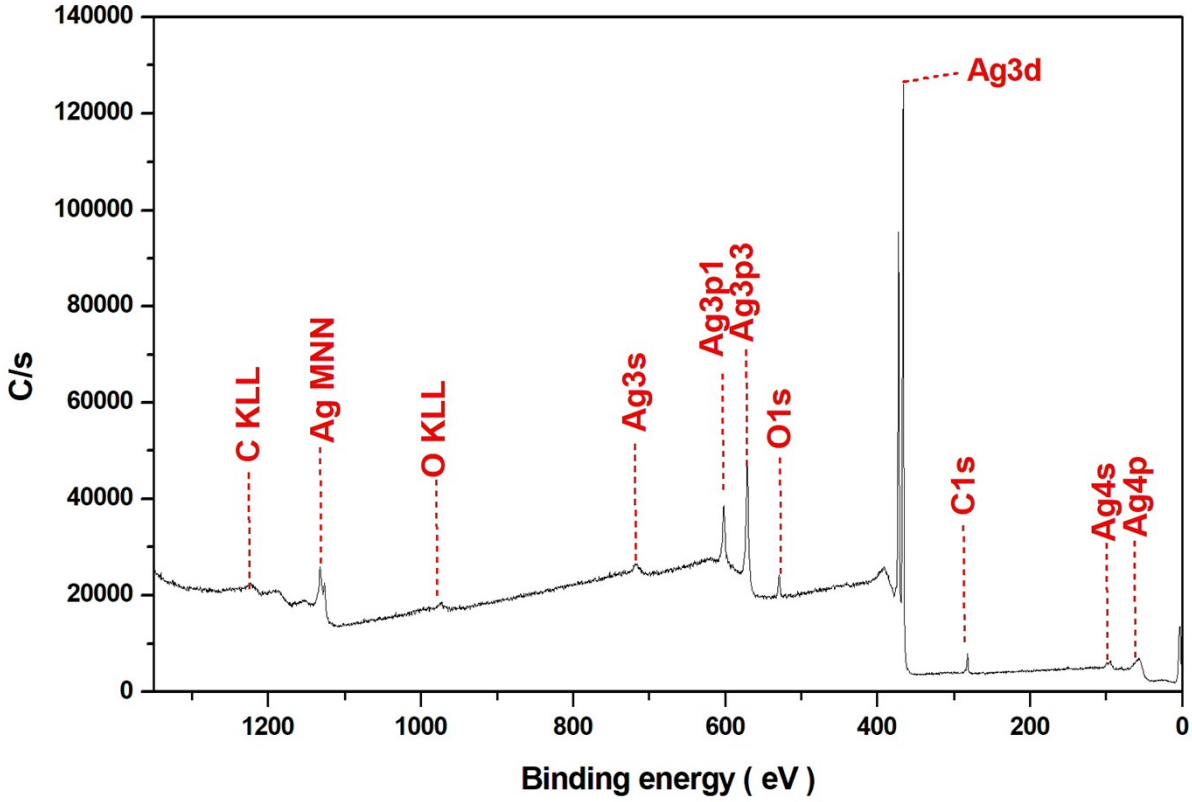


Fig. S4. (A) AFM and (B) SEM images of ion etched silicon covered with silver layer.

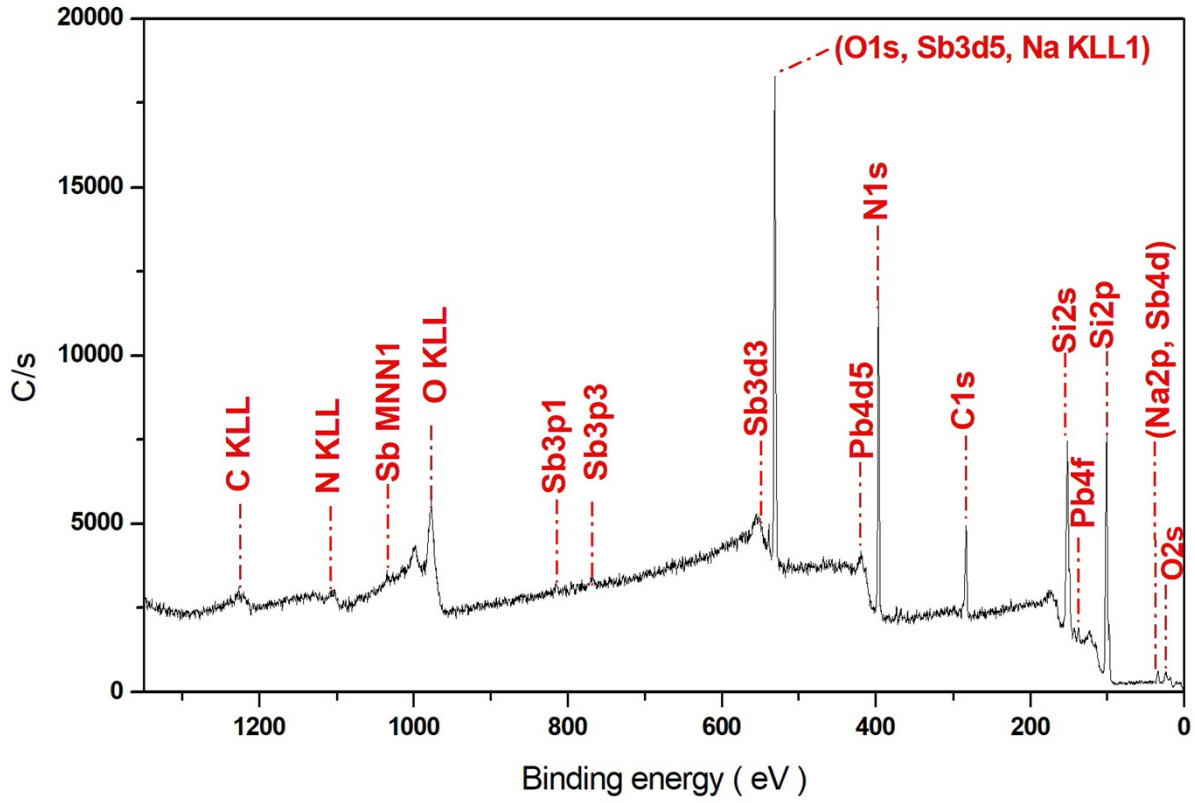
1.3. XPS analysis of Ag/PV SERS platform

A)

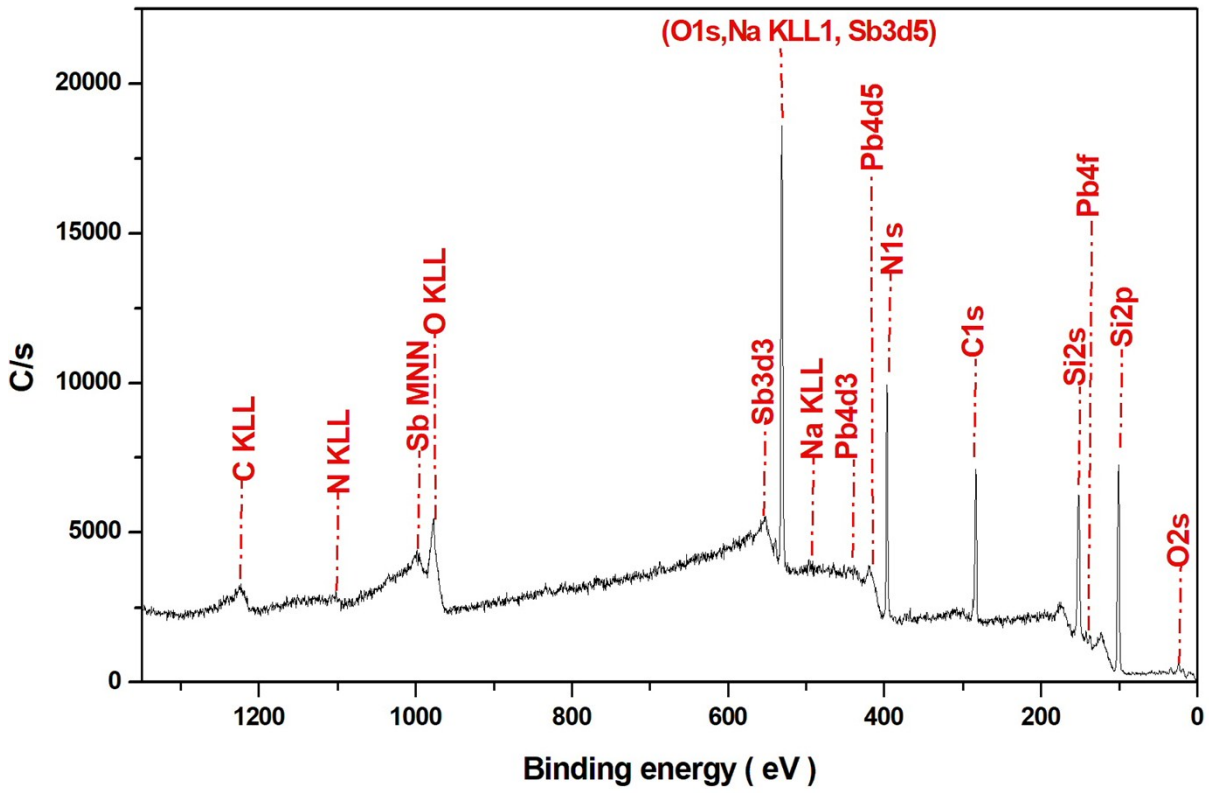
Sample 1m-type without Ag



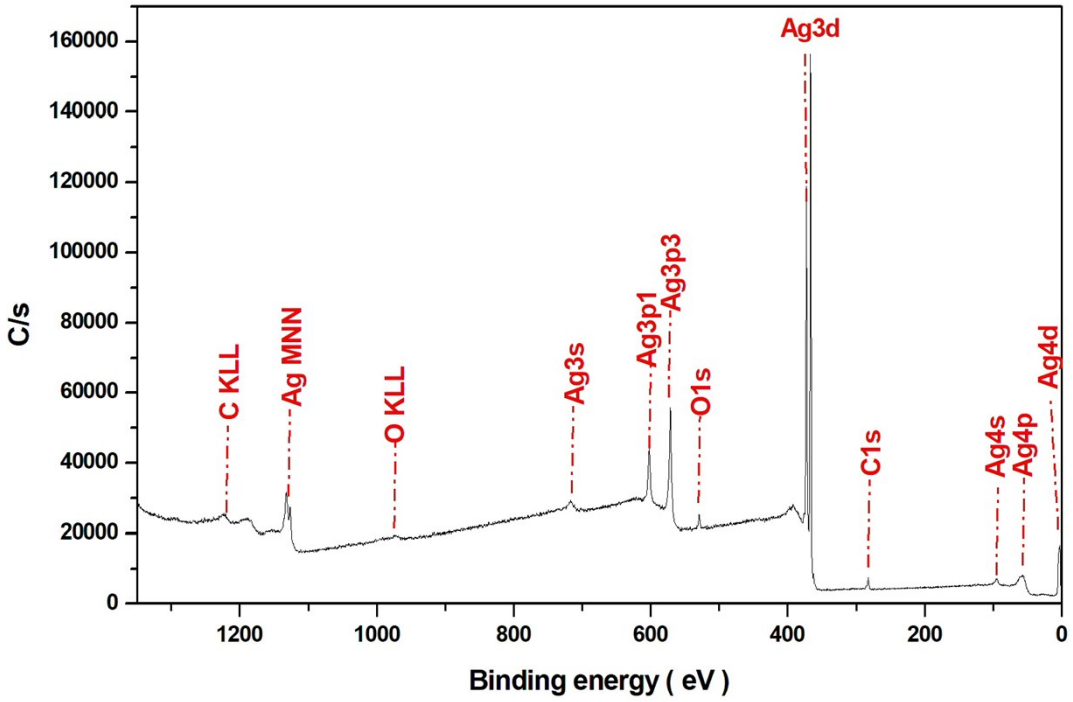
Sample 1m-type with Ag


20000
15000
10000
5000
0
C/s
1200
1000
800
600
400
200
0
Binding energy (eV)
(O1s, Sb3d5, Na KLL1)
N1s
Si2s
Si2p
(Na2p, Sb4d)
O2s
Pb4f
C1s
Pb4d5
Sb3d3
Sb3p3
Sb3p1
O KLL
Sb MNN1
N KLL
C KLL

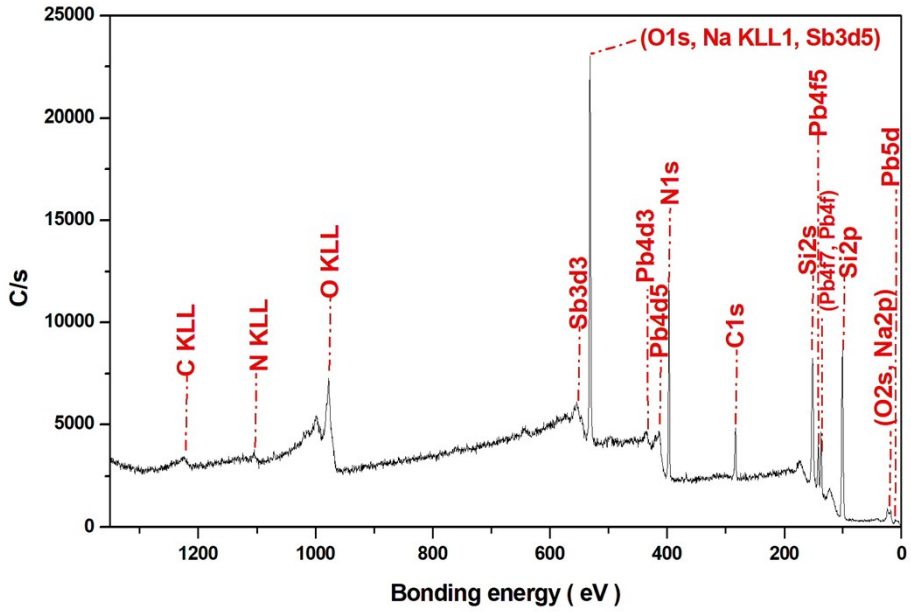
B) Sample 1-type without Ag



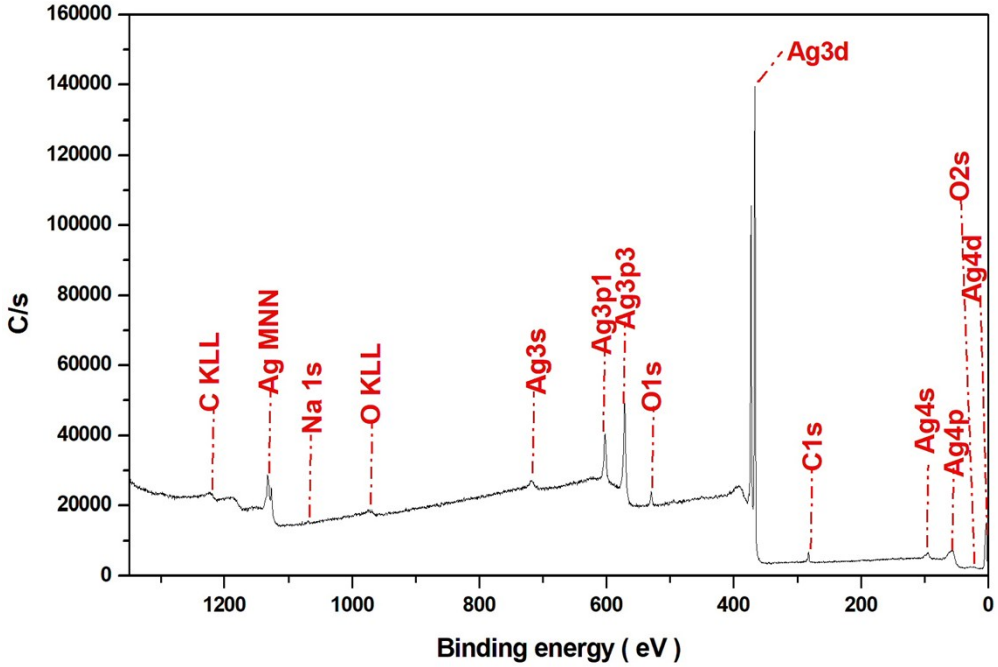
Sample 1-type with Ag


C/s
160000
140000
120000
100000
80000
60000
40000
20000
0
1200
1000
800
600
400
200
0
Binding energy (eV)
C KLL
Ag MNN
O KLL
Ag3s
Ag3p1
Ag3p3
O1s
Ag3d
C1s
Ag4s
Ag4p
Ag4d

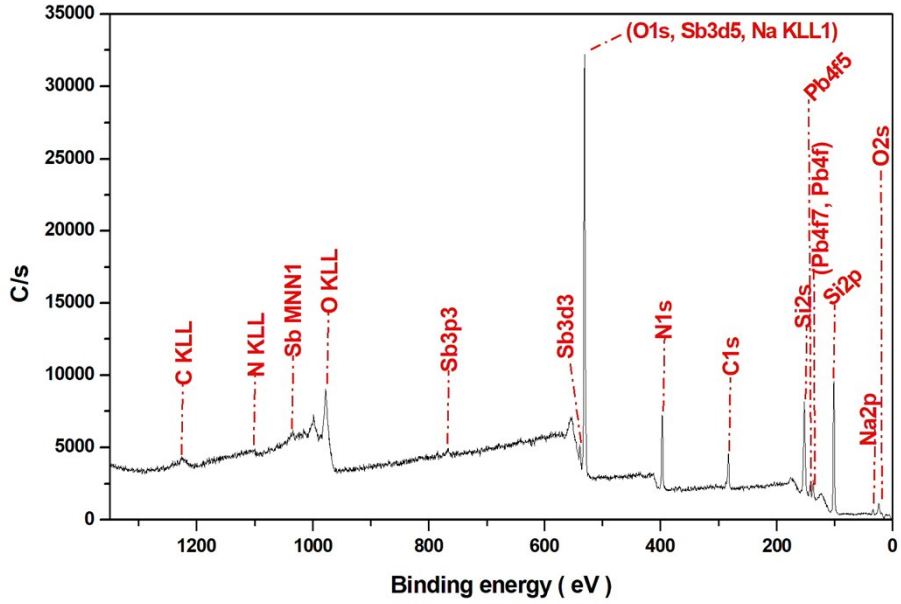
C) Sample 2-type without Ag



Sample 2-type with Ag



D) Sample 3-type without Ag



sample 3-type with Ag

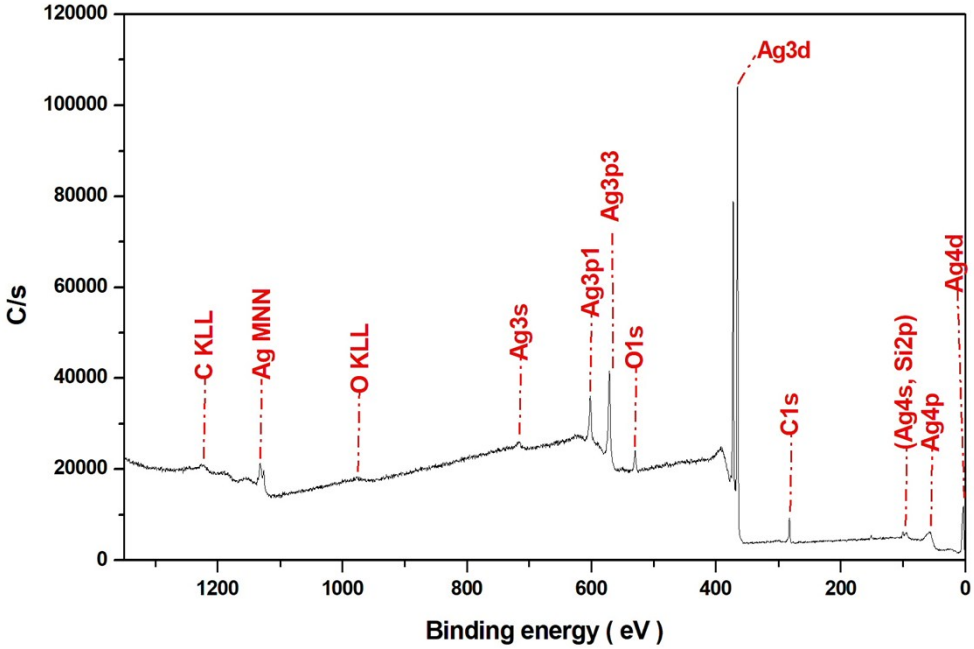


Fig. S5. XPS surveys on four SERS substrates ((A) - sample1), ((B) – sample 1m), ((C) – sample 2), and ((D) – sample 3) coated with 8 nm of Ag layer.

Table S1. Normal Raman and SERS band assignments for *p*-ATP.

Normal Raman/*p*-ATP powder	SERS/ *p*-ATP onto Ag/PV substrate	Assignments
1597	1576	νCC, 8a (a_1)
	1490	νCC + dCH, 19a (a_1)
	1435	νCC+δCH, 19b (b_2)
	1393	δCH+νCC, 3 (b_2)
	1311	δCH, 9a (a_1)
1172	1180	δCH, 9a (a_1)
	1145	δCH, 9b (b_2)
1090	1078	γCC+γCCC, 18a, (a_1)
1007	1007	γCC+γCCC, 18a, (a_1)

Abbreviations: ν = stretching, δ, γ = bending, π = wagging. Letters in parentheses indicate symmetry.

1.4. Sensitivity

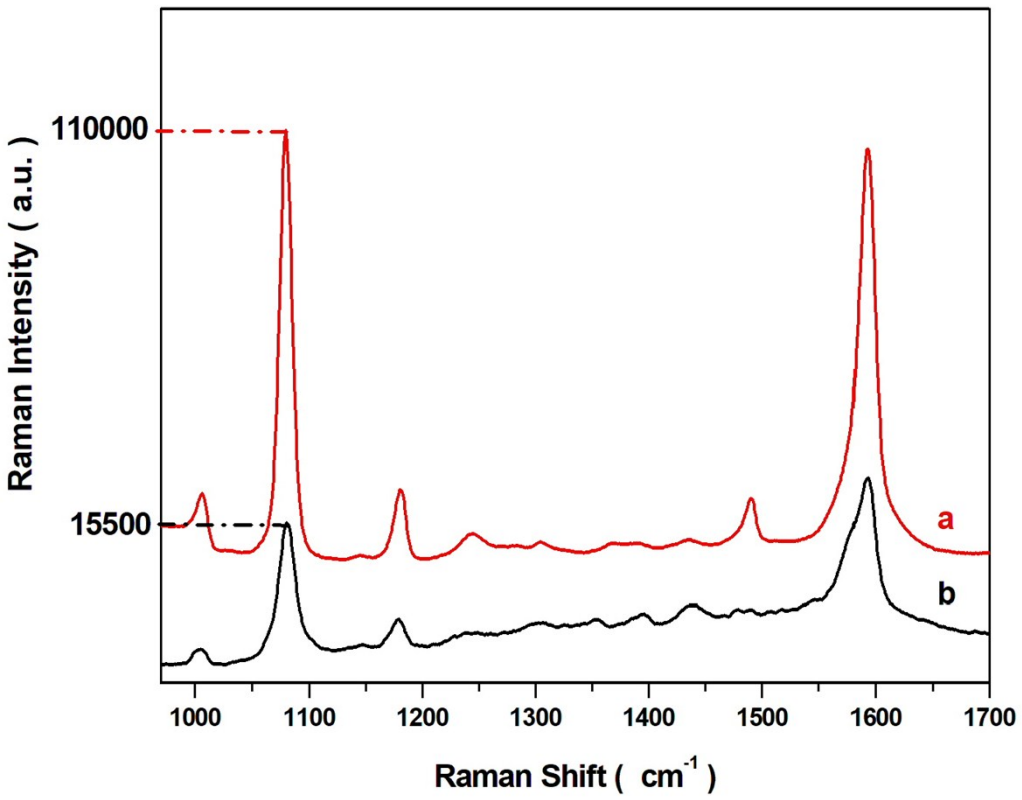
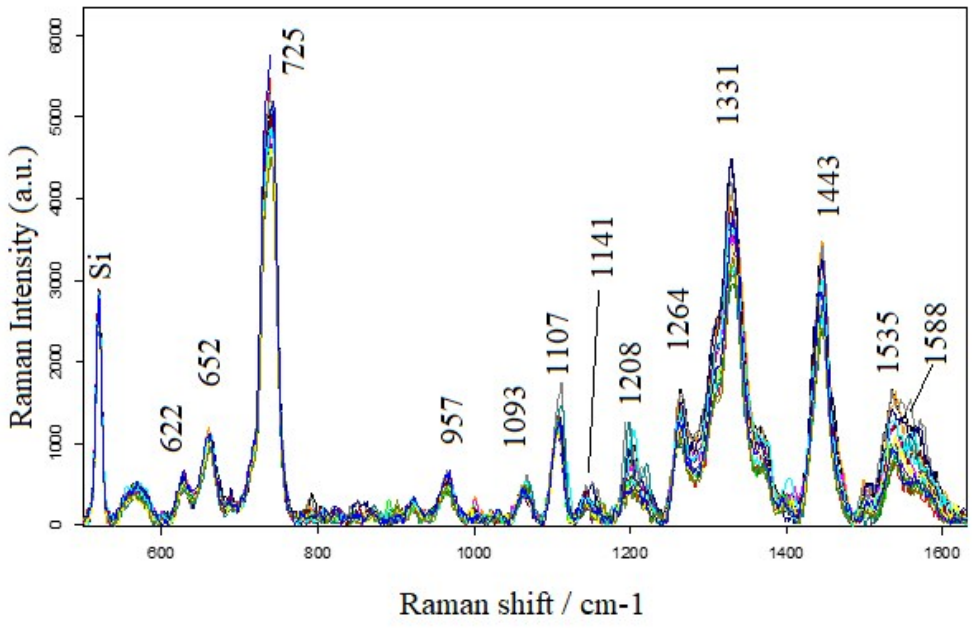


Fig. S6. The SERS spectra of *p*-ATP adsorbed onto " type 1m" SERS surface at different concentration (a) 10^{-6} M and (b) 10^{-9} M in ethanol.

2. Analytical performance of Ag/PV SERS platform

(A)



(B)

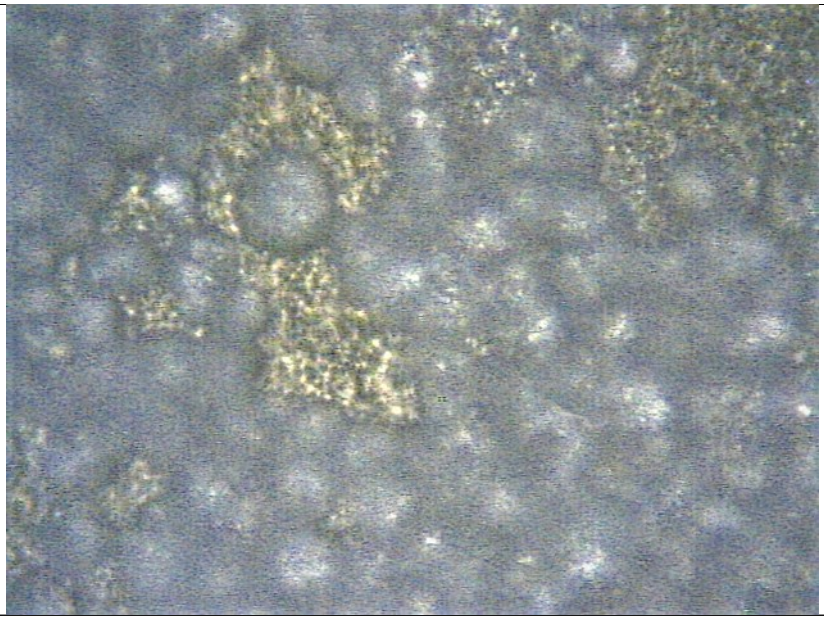


Fig. S7. The SERS spectra of *E.coli* recorded on Ag/PV substrate from randomly distributed points. For all spectra, excitation wavelength was at 785 nm, laser power was 1.5 mW, and acquisition time was only 3 seconds. (B) Microscopic image of *E.coli* deposited onto SERS-active surface (at magnification 50 X).

Table S2. Assignment of SERS bands depicted in Fig.7 for *B. subtilis* and Caki-1 (renal cancer cells).

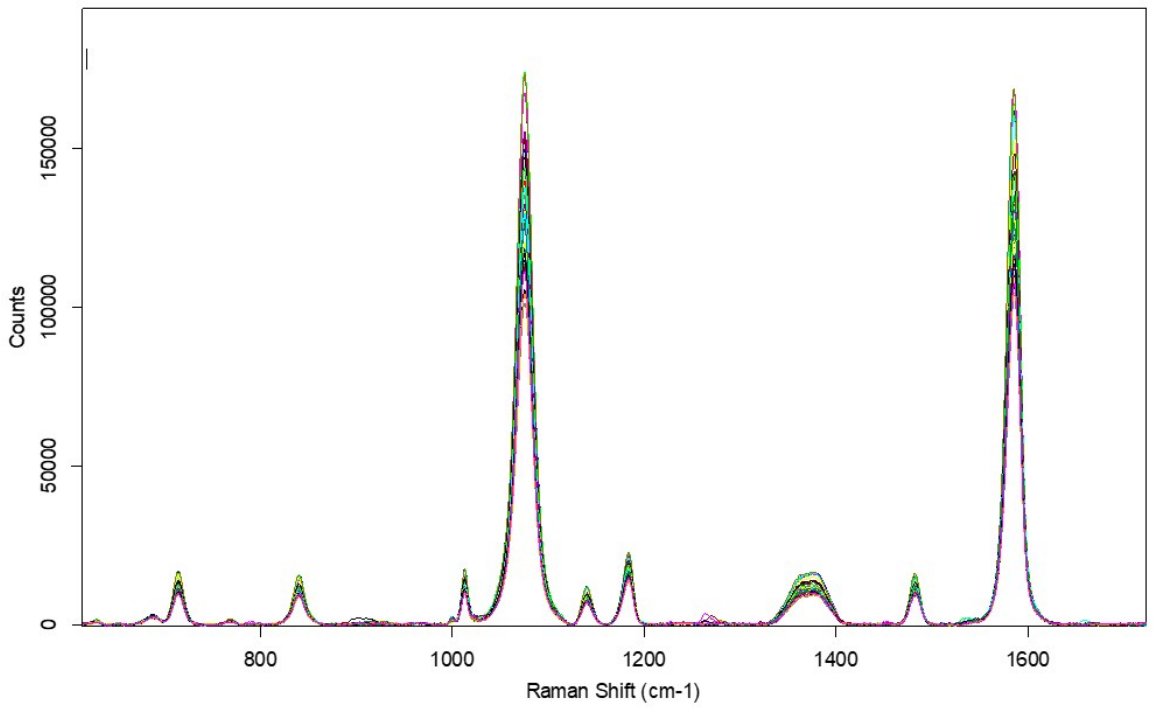
Bacillus subtilis		**Caki-1 (renal cancer cells)**	
Assignment	Range	Assignment	Range
C-O-C ring deformation	540-575	Tyr (C-C twist) (protein assignment)	652-658
Guanine, tyrosine	640-675	Trp (protein assignment) C-N head group choline $(H_3C)_3N$+(lipid assignment)	725-730
Adenine, glycoside	713-740		
Cytosine, uracil	745-790		
Symmetric breathing of tryptophan (protein assignment)	752-757	PO_2 symm (nucleic acid assignment)	785
O-P-O (RNA)	800-815	RNA backbone (nucleic acid assignment)	827
C=C deformation, C-N stretching	930-990	Tyr, Pro (protein assignment)	850
Phenylalanine, C-C aromatic ring stretching	1000-1010	Structural protein modes of tumors	890
C-C stretching (phospholipids carbohydrates),C-N stretching	1025-1060	C-C str alpha-helix, Pro, Val (protein assignment)	939
		CH_3 def (protein assignment)	956
O-P-O (DNA), C-C or C-O-C stretching (carbohydrates)	1080-1105	Phe (protein assignment)	1003
		CH_2CH_3 bending modes of lipids	1030-1032
=C-O-C= (unsaturated	1130-1145	C-N stretch (protein	1094

fatty acids in lipids)	
C-O ring, aromatic aminoacids in proteins	1150-1185
Amide III (random), thymine	1215-1295
Amide III (protein), C-H deformation	1315-1325
Adenine, guanine, CH deformation	1330-1345
COO- symmetric stretching	1390-1415
CH_2 deformation of proteins, umbrella mode of methoxyl (4)	1440-1475
Amide II	1510-1560
Adenine, guanine (ring stretching), tryptophan	1570-1595

assignment); CC str chain, C-O str (lipid assignment); PO_2 symm (nucleic acid assignment)	
C-N str bk (protein assignment); Porphyrin (lipid assignment)	1128
Tyr C-H in plane (protein assignment); T (nucleic acid assignment)	1170-1172
C-C_6H_5 str in phenylalanine tyrosine (protein assignment)	1212
Amide III (beta sheet), (protein assignment)	1245
Amide III (random coil) (protein assignment); CH= CH def (lipid assignment)	1267-1270
purine bases of DNA (nucleic acid assignment)	1325
A,G (nucleic acid assignment)	1345
Sphingoglycolipids (lipid assignment)	1373
structural protein modes of tumors (protein assignment)	1452
A,G (nucleic acid assignment)	1552

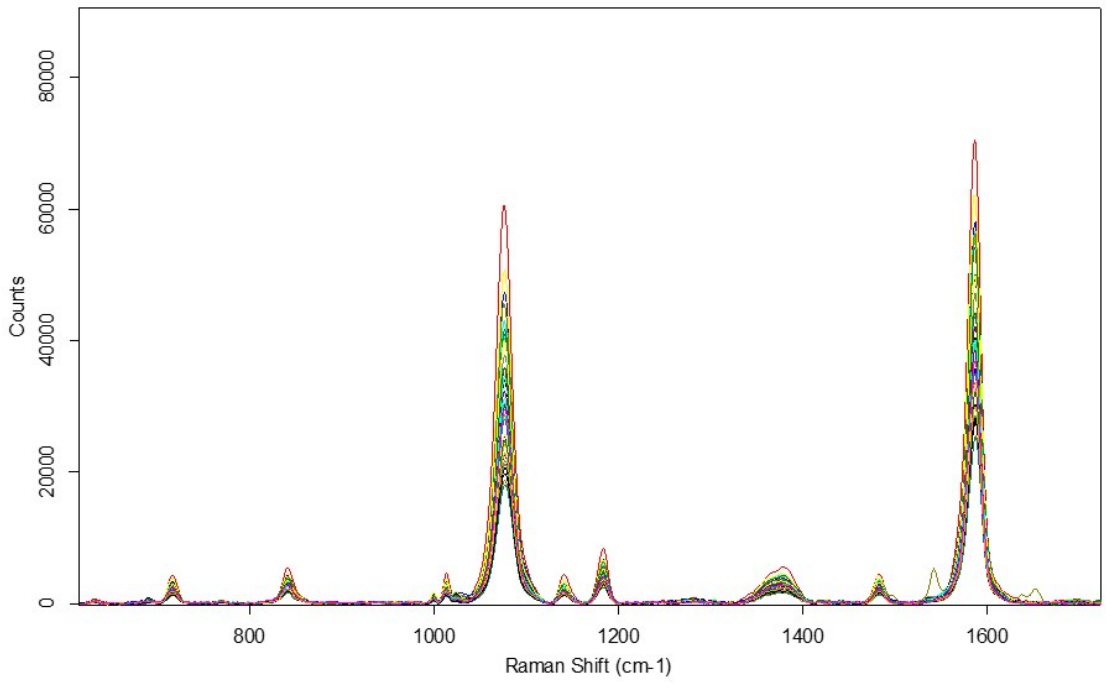
	Phe, Tyr (protein assignment)	1597-1600
	C≡C str of Tyr and Trp (protein assignment)	1616-1618
	Amide I (protein assignment); C=C str (lipid assignment)	1657-1695

3. Reproducibility and sensitivity of SERS substrates.



(A) sample 1m-type

(B) Sample 1-type



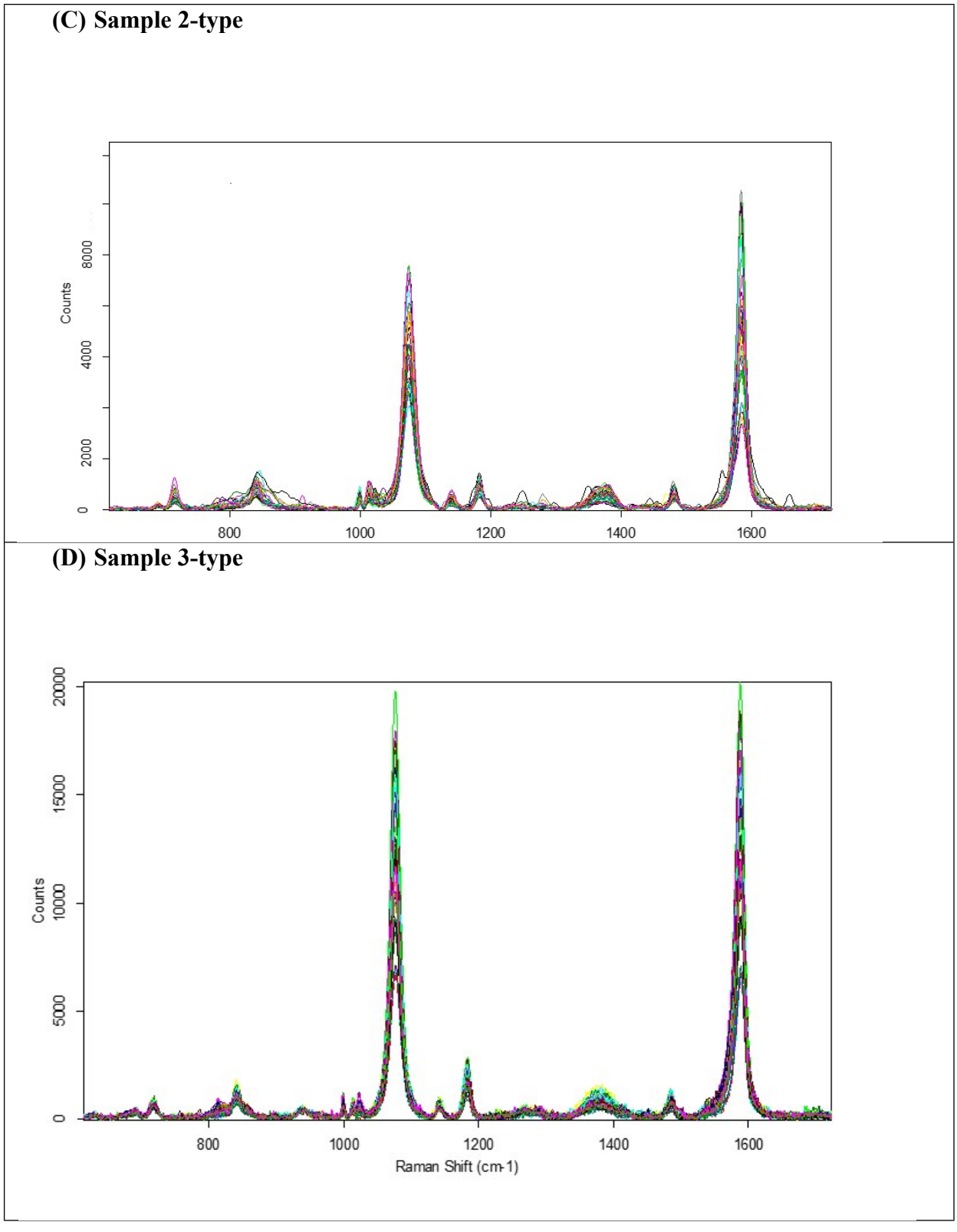


Fig. S8. The representative SERS spectra *p*-ATP of concentration 10^{-6} M in ethanol recorded from 40 different spots on the four different SERS surfaces (type 1m, 1, 2, and 3) using mapping mode. The spectra were collected over an area 10 x 20 µm with 1.6 steps µm (40 spectra are shown). Each point in the map was recorded using 1.5 mW of 785 nm excitation with 18 seconds integration times.

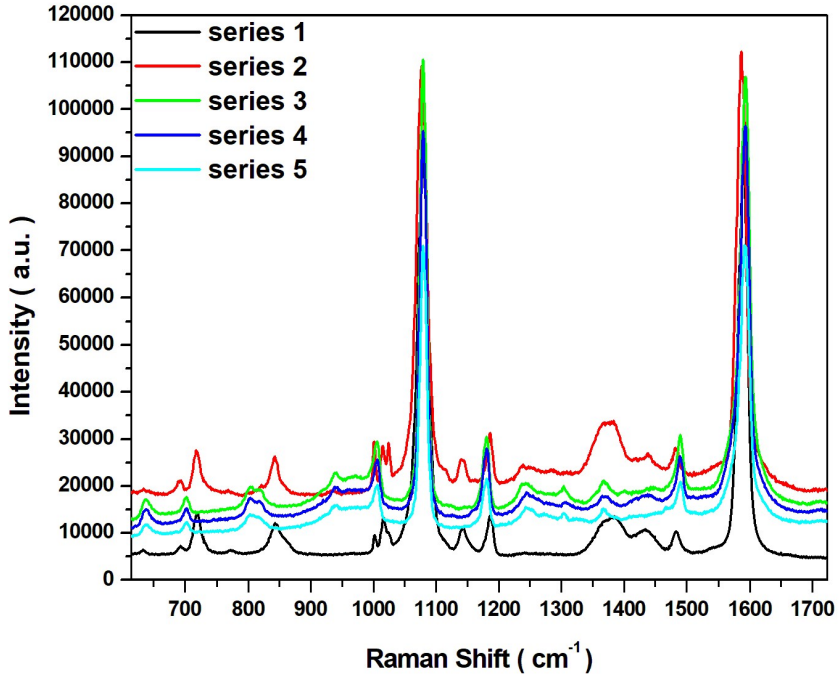


Fig. S9. The representative SERS spectra *p*-ATP of concentration 10^{-6} M in ethanol recorded from 40 different spots on the five different SERS surfaces prepared separately. The spectra were collected over an area 10 x 20 µm with 1.6 steps µm (40 spectra are shown). Each point in the map was recorded using 1.5 mW of 785 nm excitation with 18 seconds integration times.